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Direct Inversion of the Iterative Subspace (DIIS) convergence accelerator for crystalline solids employing Gaussian basis sets.

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Abstract When dealing with crystalline solids, convergence of iterative procedures such as self-consistent field (SCF) or coupled-perturbed equations is often more difficult than in the case of molecular systems, specially when a local basis set of atom-centred Gaussians is adopted. Reasons are usually to be found in the close packing of atoms and peculiar chemical characters, such as metallic bond.

In this work, a periodic implementation of the Direct Inversion of Iterative Subspace (DIIS) method for crystalline solids is presented for SCF and electric field response up to second order. The error vectors are computed in reciprocal space, and implemented for the energy, polarizability and up to second hyperpolarizability. The performance of different DIIS flavors is benchmarked on a representative set of 42 systems including metallic, ionic, molecular and covalent crystals, bulk crystals, surfaces and nanotubes, adopting all-electron basis sets as well as pseudopotentials. Interestingly, it is seen that the error vectors evaluated in the central (γ) point of the Brillouin zone are sufficient in all cases for an optimal DIIS performance.

1 Introduction

The Direct Inversion of the Iterative Subspace (DIIS) is a powerful convergence acceleration technique that has been key in fostering the development of quantum chemistry in the last 30 years. Its application to iterative procedures in codes dealing with crystalline periodic systems requires a careful adaptation, due to the different chemistry of the systems under study, which we discuss in this paper.

The introduction of convergence acceleration methods represents a cornerstone in the history of quantum chemistry. Not only such techniques allow to reach much more rapidly the desired result, but also considerably stabilize the iterative procedure and, eventually, lead more securely to the lowest-energy state. Pulay's original DIIS formulation[1,2] is also known as Commutator-DIIS (CDIIS), and

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it rapidly proved more successful than other other recipes such as Broyden,[3] Anderson[4] or the epsilon algorithm.[5]

The literature regarding molecular implementations of DIIS for Self-Consistent Field (SCF) is sizeable. Recipes alternative to CDIIS have been proposed by different authors.[6–10] These differ in the definition of the error functional (*vide infra*) that might include the energy or not, and can allow negative coefficients or not in the expansion. As for trial-vector approaches for derivatives of Hartree–Fock and DFT methods, its introduction dates back to the work of Pople *et al.*[11] which, according to Ref. [1], actually gave the inspiration to develop DIIS.

As for periodic systems, the literature is less rich. An accurate analysis of the performance of DIIS in the SCF convergence of solids, with a focus on metals, is found in the works of Kresse and Furthmüller [12] in the context of a plane-wave basis set. Problems of metallic solids, such as charge sloshing in the proximity of the gamma point of the Brillouin zone, are discussed therein.

In this contribution the implementation of DIIS for periodic boundary condition (PBC) methods employing an atom-centered Gaussian basis set is presented for SCF and CPHF/KS up to second order. The method has been implemented in the CRYSTAL17 program.[13]

2 Theory

2.1 DIIS for the Self-Consistent Field (SCF) iterations

In DIIS, at each cycle n of the SCF, instead of the Fock matrix $\mathbf{F}_n = \mathbf{F}[\mathbf{D}_{n-1}]$ constructed from the density matrix \mathbf{D}_{n-1} , an averaged effective Hamiltonian is generated as a linear combination of the older Fock matrices:

$$\bar{\mathbf{F}}_n = \sum_{i=1}^n c_i \mathbf{F}_i \quad . \quad (1)$$

The c_i coefficients are obtained by minimizing a suitable error measure $|\mathbf{e}_i\rangle$, under the constraint that $\sum_i c_i = 1$. This is obtained by solving the linear equation system

$$\begin{pmatrix} \mathbf{e} & \mathbf{1}^T \\ \mathbf{1} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix} \quad (2)$$

where \mathbf{e} is an error matrix having the size of the iterative space considered – equal or smaller than n . The error matrix is defined through scalar products $e_{nm} = \langle \mathbf{e}_n | \mathbf{e}_m \rangle$, defined as $\langle \mathbf{A} | \mathbf{B} \rangle = \text{Tr}[\mathbf{A}^\dagger \mathbf{B}]$.

To better understand how the method works, we note that eq. (2) corresponds to a Newton step $\mathbf{c} = \mathbf{H}^{-1} \mathbf{g}$ in coefficients space minimizing the Lagrangian

$$\mathcal{L}^{DIIS}(\mathbf{c}, \lambda) = \sum_i \sum_j c_i c_j e_{ij} + \lambda \left(1 - \sum_i c_i \right) \quad (3)$$

Gradients with respect to coefficients are $g_i = \sum_j c_j e_{ij} - \lambda$ and the Hessian $H_{ij} = e_{ij}$. By setting the initial guess condition to $\mathbf{c} = 0$, and including derivatives with respect to λ , Eq. (2) is obtained. Hence, in presence of multiple minima, DIIS leads to the local minimum closest to $\mathbf{c} = 0$.

In the case of periodic systems, we define the DIIS error matrix of Eq. (2) as a back-Fourier transform of reciprocal space quantities

$$e_{nm} = \frac{1}{N_k} \sum_k \langle \mathbf{e}_n(\mathbf{k}) | \mathbf{e}_m(\mathbf{k}) \rangle \quad (4)$$

where \mathbf{k} is a vector in the first Brillouin zone.

By extending the CDIIS methods[1] to reciprocal space we obtain

$$\mathbf{e}_n(\mathbf{k}) = \mathbf{F}_n(\mathbf{k})\mathbf{D}_n(\mathbf{k})\mathbf{S}(\mathbf{k}) - \mathbf{S}(\mathbf{k})\mathbf{D}_n(\mathbf{k})\mathbf{F}_n(\mathbf{k}) \quad (5)$$

where $\mathbf{S}(\mathbf{k})$ is the overlap matrix. In the case of periodic systems, the CDIIS formulation is particularly convenient, if compared to Eq. (11) below, since it allows the number of occupied orbitals in a given \mathbf{k} point to change from one iteration to another. Hence, in the case of a conducting system, or of an insulator that passes through a conducting state during the SCF iterations, it permits fluctuations of electrons across the Brillouin zone.

Eq. (5) is straightforwardly extensible to Symmetry-Adapted Crystalline Orbitals (SACO): if, in each \mathbf{k} -point, the Fock matrix can be made block-diagonal according to irreducible representations (IRREPs) μ , [14] then the error can be evaluated separately for each μ :

$$\begin{aligned} |\mathbf{e}_n(\mathbf{k}, \mu)\rangle &= \mathbf{F}_n(\mathbf{k}, \mu)\mathbf{D}_n(\mathbf{k}, \mu)\mathbf{S}(\mathbf{k}, \mu) \\ &\quad - \mathbf{S}(\mathbf{k}, \mu)\mathbf{D}_n(\mathbf{k}, \mu)\mathbf{F}_n(\mathbf{k}, \mu) \quad . \end{aligned} \quad (6)$$

All the matrices have the size of the SACOs in the IRREP, with significant advantages in terms of computing and storage resources. By introducing d_μ as the multiplicity of IRREP μ , errors become

$$e_{nm} = \frac{1}{N_k} \sum_{k, \mu} d_\mu \langle \mathbf{e}_n(\mathbf{k}, \mu) | \mathbf{e}_m(\mathbf{k}, \mu) \rangle \quad . \quad (7)$$

Note that, during the SCF, a given IRREP could be occupied by a different number of electrons in different iterations, or even unoccupied (in which case the error vector would be null). Fortunately, this happens only in early cycles when all other error vectors are very large, hence this occurrence is never harmful in practice.

A numerically robust equation solver allows inclusion of the whole history in Eq. (2) without linear dependence problems. Although DIIS is ordinarily employed only within the convergence region, we found here that including a longer list of iterations does speed up convergence. The algorithm presented discards an older iterations i only when the absolute value of corresponding coefficient c_i in Eq. (1) is below 10^{-8} . Intel's MKL[15] libraries were used.

Problems in SCF of conducting systems can be rationalized as a charge sloshing between \mathbf{k} -vectors with long wavelengths.[12] A solution is to introduce proper \mathbf{k} -point weights g_k (see Eq. (64) in Ref. [12]) so that errors from short-wavelength \mathbf{k} -points become more relevant. Eq. (4) becomes:

$$e_{nm} = \frac{1}{N_k} \sum_k g_k \langle \mathbf{e}_n(\mathbf{k}) | \mathbf{e}_m(\mathbf{k}) \rangle \quad . \quad (8)$$

with

$$g_k = \frac{k^2 + k_1^2}{k^2} \quad . \quad (9)$$

k is the length of the vector \mathbf{k} . The choice of the parameter k_1 is defined “relatively unimportant” in Ref. [12], and our observations confirm this statement. k_1 is here set at a value of 1.2 Bohr^{-1} .

It is also possible to consider only the errors in the Γ point of the Brillouin zone ($\mathbf{k} = 0$)

$$e_{nm} = \langle \mathbf{e}_n(0) | \mathbf{e}_m(0) \rangle \quad (10)$$

which can be interpreted as an extreme case of charge sloshing, in which the weighting factors are so different that only Γ -point contributions survive. Eq. (10) has the advantage that it requires only one error vector at each iteration, instead of N_k , thus dramatically reducing the requirements in terms of disk/memory space and I/O overhead, specially when combined with the symmetry factorization of Eq. (6).

2.2 DIIS for Coupled-Perturbed Hartree-Fock/Kohn-Sham (CPHF/KS) iterations

We now move to the extension of the periodic DIIS procedure to the case of first-order CPHF/KS treatment in crystalline solids. We refer here to the response to an external electric field \mathcal{E} , as developed and implemented in CRYSTAL[16] for polarizability and first-hyperpolarizability tensors.

A possible form for the SCF error vector, different from (5), is obtained as the off-diagonal block of the Fock matrix in the basis of crystalline orbitals $\mathbf{G}_n(\mathbf{k})$ [17]

$$|\mathbf{e}_n(\mathbf{k})\rangle = \mathbf{G}_n^{\text{OV}}(\mathbf{k}) = \mathbf{C}_n^{\text{O}\dagger}(\mathbf{k}) \mathbf{F}_n(\mathbf{k}) \mathbf{C}_n^{\text{V}}(\mathbf{k}) \quad (11)$$

which is entirely equivalent to Eq. (5) if bands occupation is stable across SCF cycles. O and V superscripts indicate *occupied* and *virtual* blocks of \mathbf{C}_n , respectively. \mathbf{C}_n is the matrix of eigenvectors of \mathbf{F}_n . The error vector (11) contains gradients of the total energy with respect to an orbital rotation between occupied and virtuals.[17] This shows why DIIS has general difficulties in working together with artificial shiftings of the virtual energy levels, even though their simultaneous use is sometimes mentioned in literature.[18] Level shifting is turned off in our implementation.

The error vector for the CPHF/KS iterative procedure is obtained by differentiating Eq. (11) with respect to an electric field cartesian component \mathcal{E}_u at zero field:

$$\begin{aligned} |\mathbf{e}_n^{(u)}(\mathbf{k})\rangle &= \left. \frac{\partial[\mathbf{G}_n^{\text{OV}}(\mathbf{k})]}{\partial \mathcal{E}_u} \right|_{\mathcal{E}=0} \\ &= \left[\mathbf{G}_n^{(u)}(\mathbf{k}) + \mathbf{U}_n^{(u)\dagger}(\mathbf{k}) \epsilon_n^{(0)}(\mathbf{k}) + \epsilon_n^{(0)}(\mathbf{k}) \mathbf{U}_n^{(u)}(\mathbf{k}) \right]^{\text{OV}} \end{aligned} \quad (12)$$

where

$$\mathbf{G}_n^{(u)}(\mathbf{k}) = \mathbf{C}^{(0)\dagger}(\mathbf{k}) \mathbf{F}^{(u)}(\mathbf{k}) \mathbf{C}^{(0)}(\mathbf{k}) + \mathbf{\Omega}_u(\mathbf{k}) \quad , \quad (13)$$

$\epsilon_n^{(0)}(\mathbf{k})$ are unperturbed eigenvalues, and $\mathbf{F}^{(u)} = \mathbf{F}[\mathbf{D}^{(u)}]$.

Here $\mathbf{U}^{(u)}(\mathbf{k})$ determines the first-order perturbed coefficients along direction u , since the field-perturbed coefficients are expressed in terms of the unperturbed ones, $\mathbf{C}^{(u)}(\mathbf{k}) = \mathbf{C}^{(0)}(\mathbf{k}) \mathbf{U}^{(u)}(\mathbf{k})$ and then combined to yield the field-perturbed density $\mathbf{D}^{(u)}$. The last term on the r.h.s. of Eq. (13) – $\Omega_u(\mathbf{k})$ – is the electric field operator and its explicit form has been discussed in detail in a number of papers.[16,19] It contains, as in the molecular case, the matrix of dipole moments, plus terms related to the derivative of the overlap matrix and coefficients with respect to the reciprocal space vector \mathbf{k} which are peculiar to the periodic case due to the special form of the operator [20,21]. Eq. (12) is easily related with Eq. (41) of Ref. [16], considered that $\mathbf{U}^{(u)\dagger}(\mathbf{k}) = -\mathbf{U}^{(u)}(\mathbf{k})$ (which results from differentiating the normalization condition).

Second-order CPHF/KS gives access to the second hyperpolarizability (γ) through double differentiation with respect to the electric field[16] and Raman intensities.[19] The error vector is obtained, in analogy with Eq. (12), as:

$$\begin{aligned} |\mathbf{e}_n^{(t,u)}(\mathbf{k})\rangle &= \left. \frac{\partial^2 [\mathbf{G}_n^{\text{OV}}(\mathbf{k})]}{\partial \mathcal{E}_t \partial \mathcal{E}_u} \right|_{\mathcal{E}=0} = \\ & \left[\mathbf{G}_n^{(t,u)}(\mathbf{k}) + \mathbf{U}_n^{(t,u)\dagger}(\mathbf{k}) \epsilon_n^{(0)}(\mathbf{k}) + \epsilon_n^{(0)}(\mathbf{k}) \mathbf{U}_n^{(t,u)}(\mathbf{k}) \right]^{\text{OV}} \\ & + \mathcal{P}_{t,u} \left[\mathbf{U}_n^{(t)\dagger}(\mathbf{k}) \mathbf{G}_n^{(u)}(\mathbf{k}) + \mathbf{G}_n^{(u)}(\mathbf{k}) \mathbf{U}_n^{(t)}(\mathbf{k}) \right]^{\text{OV}} \end{aligned} \quad (14)$$

where

$$\mathbf{G}^{(t,u)}(\mathbf{k}) = \mathbf{C}^{(0)\dagger}(\mathbf{k}) \mathbf{F}^{(t,u)}(\mathbf{k}) \mathbf{C}^{(0)}(\mathbf{k}) + i \mathcal{P}_{t,u} \frac{\partial \mathbf{U}_n^{(t)}(\mathbf{k})}{\partial \mathbf{k}_u} \quad (15)$$

and $\mathbf{C}^{(u,v)}(\mathbf{k}) = \mathbf{C}^{(0)}(\mathbf{k}) \mathbf{U}^{(u,v)}(\mathbf{k})$ are the second-order field-perturbed coefficients. Note the last term on the r.h.s. of Eq. (15), that is specific of periodic systems and, again, due to the particular form of the electric field operator.[20] Eqs. (14)–(15) are to be related to Eq. (43) of Ref. [16].

3 Results

A test set of 42 periodic systems has been designed, grouped according to physico-chemical character. Such set covers different basis sets sizes and types (all-electron or with pseudopotentials), different dimensionalities (1D, 2D and 3D), employing Hartree-Fock and different functionals (LDA, PBE, PBE0, B3LYP, HSE06). The systems are described in detail in supplementary information, along with inputs. The CRYSTAL17[13] code has been used for all calculations. Superposition of atomic densities was taken as SCF initial guess. Convergence was set to $10^{-10} E_h$ for the SCF total energy, and to 10^{-4} Bohr^3 on the polarizability value for CPHF/KS. For second-order CPHF/KS equations, convergence is not evaluated directly on the second hyperpolarizability γ , that is costly to evaluate at each cycle, but rather to a pseudo-energy derivative.[16] Cases of “false convergence” can happen, when the DIIS weight given to the last iteration is too small. When smaller than 10^{-5} , a step with Fock damping is performed instead of DIIS. A high Fock mixing (up to

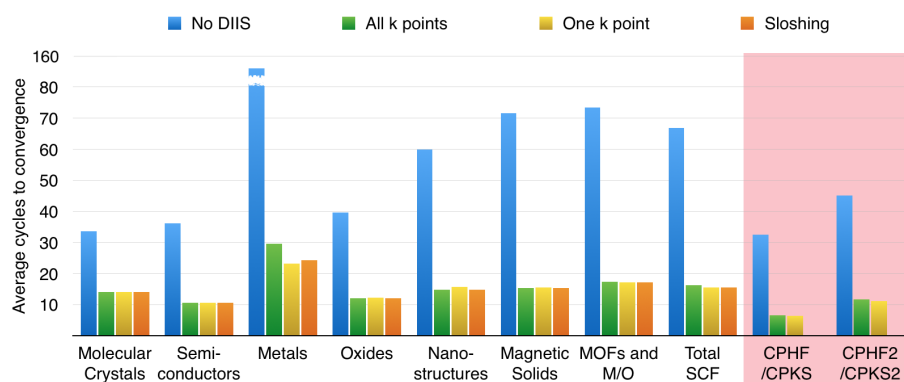


Fig. 1 Performance of the DIIS variants, compared to the non-accelerated code, for the test set of 42 systems introduced in this work. In the first 7 blocks, results for the SCF are presented grouped by systems with chemical and structural affinities (6 systems per group). In the “Total SCF” column an overall average of the result for the 42 systems is reported. MOF stands for Metal-organic Frameworks, M/O for Metal/Oxide interfaces. The two rightmost columns (with a colored background) report the averaged performance over a suitable subset of 25 systems for the coupled-perturbed procedure at first- and second-order (CPHF and CPHF2).

90%) and eigenvalue shifts have been activated when needed in order to converge the non-DIIS cases. No shift is applied with DIIS. Full detail on inputs can be found in supplementary information.

In Figure 1 we report the results of performance tests. The average speedup in SCF cycles to convergence, with respect to the non-accelerated case, is more than a factor of 4, ranging from about 2 for molecular crystals to more than 6 for metals. The effect of different treatments of reciprocal space errors appears overall minor, with the computationally most convenient choice (1 k point) being equally or more efficient than schemes sampling the entire Brillouin zone. The performances for CPHF/KS at both orders, as obtained on a subset of 25 systems, are similar. In Figure 2, as an exemplary case, the detail of performances for single-layer MoS₂ (test #29) is shown. Even if following slightly different paths in the beginning, both DIIS-accelerated methods behave similarly and considerably faster than the non-accelerated case. Oscillations in the first CPKS2 iterations are here impressively high, reaching 10^{12} .

In 41 out of the 42 tests the final energy is the same, within accuracy, for all schemes. The outlier is the case of bulk Gd, presented in detail in Figure 3: the “All k points” and “Sloshing” schemes converge to a higher energy. The non-accelerated SCF reaches the correct ground state, but taking 180 cycles more than Γ -point DIIS. Insight is provided – in the bottom panel of Figure 3 – following the evolution of the Fermi level during the SCF. Very strong oscillations are observed in all cases in the first 10 cycles, but the “wrong” cases show fluctuations going much further (up to cycle 75).

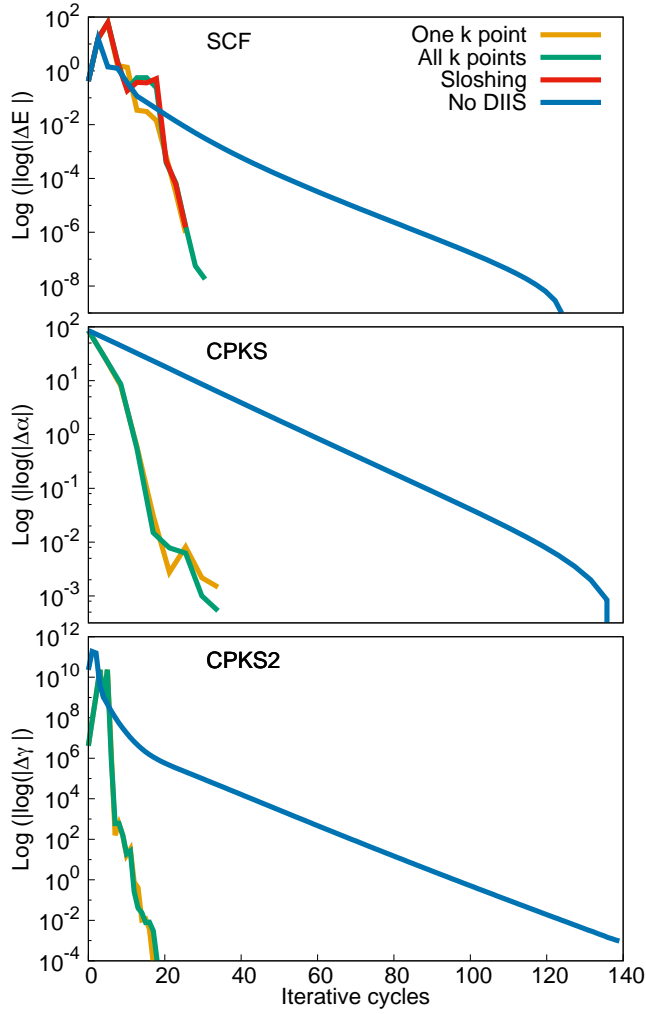


Fig. 2 Effect of DIIS accelerators in the case on single-layer MoS_2 (test #29). Convergence of total energy (top panel), polarizability (middle panel) and second hyperpolarizability (bottom panel) are reported with respect to converged values as a function of iterative cycles.

4 Conclusions

The DIIS method for accelerating self-consistent procedures in ab initio calculation for crystalline solids has been implemented in the CRYSTAL code, that uses a Gaussian basis sets. The cases of SCF, and CPHF/KS up to second order, are covered. Performance with respect to non-accelerated procedures is significant, and the sampling of the Γ point of reciprocal space for DIIS errors appears to be the best choice. Future possible developments include extension to other DIIS variants,[22, 6,8–10] and implementation of DIIS-accelerated geometry optimizers.[23]

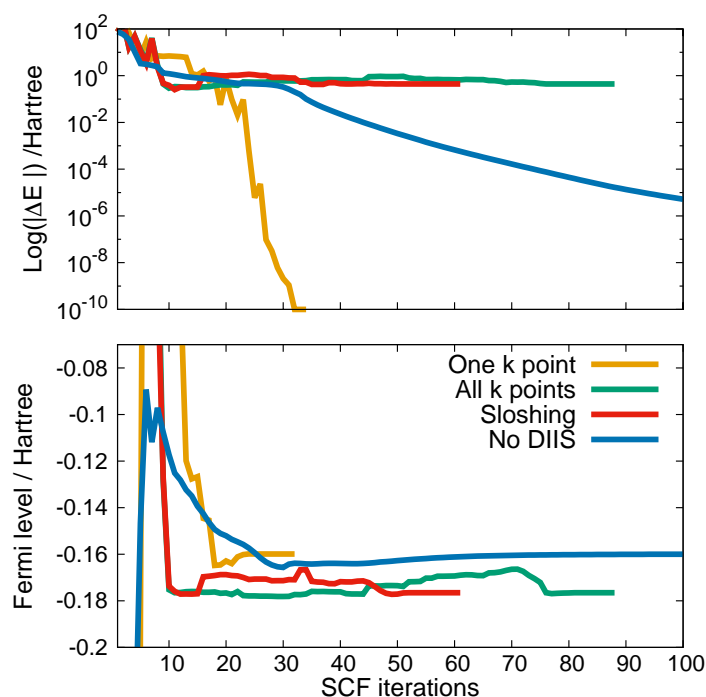


Fig. 3 Convergence of total energy with respect to the lowest energy state (top panel) and variation of the Fermi level (bottom) for bulk solid Gd as a function of SCF iterations. Data are reported for different variants of the DIIS method, including the non-accelerated case (NO DIIS), which converges in 213 iterations.

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